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13. ABSTRACT (Maximum 200 words)

Research has been conducted on two projects: intrinsic chemical markers and water-activated chemical heaters. It has recently been discovered at the Army's Natick, Massachusetts Research, Development & Engineering Center that certain chemical substances produced as a result of the thermal treatment of food can serve as chemical indicators of sterility. The relationship between marker formation and bacteria destruction has been established through mathematical models and verified experimentally and by computer simulation of different thermoprocessing profiles. It has also been shown at Natick that packaged foods can be readily heated using a flameless chemical heater. Kinetics and calorimetric studies have been carried out to determine which physical and chemical factors are most responsible for the energy released when water reacts with a magnesium-iron mixture in the presence of electrolyte in the heater. A mechanism for reaction and heat generation has been developed which can serve as the basis for a dynamical model of the heater. On the basis of this mechanism, a strategy has been developed for suppression of the concomitantly generated H_2 gas.

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KINETICS AND MECHANISM OF CHEMICAL MARKER FORMATION
AND WATER-ACTIVATED HEAT GENERATION

FINAL REPORT

KENNETH KUSTIN

MAY 1, 1994

BRANDEIS UNIVERSITY

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Table of Contents

1. Foreword

This report covers research on two projects concerned with improving thermal processing of rations and ration components and heating of individual rations, group rations, medical supplies, and even friend/foe identification devices. A chemical marker is a substance produced in food as a result of heating. Such a chemical compound, the amount of which is responsive to the time and temperature of heating, can be a useful adjunct to aseptic food processing by ensuring that sufficiently high temperatures have been maintained long enough to destroy harmful microorganisms (Kim and Taub, 1993). The Sustainability Directorate has been actively involved in developing the use of intrinsic chemical markers as indicators of the extent of bacterial destruction. The research reported here has contributed to the identification of intrinsic chemical markers and to the study of the kinetics of their formation; it has related the dynamics of marker formation to the progress and extent of bacterial destruction.

Water-activated chemical heaters, sometimes referred to as Flameless Ration Heaters (FRH), were used with great success in Operation Desert Shield. Their usage would be greatly extended by controlling the rate of heat release and by eliminating or significantly reducing the generation of dihydrogen gas (H_2), a by-product of the iron-activated magnesium-water reaction which forms the basis of the FRH. Heating multiple rations, in the form of stacked trays, for example, would be compromised by the generation of flammable dihydrogen in confined spaces. Our investigations, through calorimetric and manometric methods, of the kinetics of the basic reaction have led to the formulation of a mechanism of this reaction, and this mechanism has, in turn, led to successful strategies of H_2 suppression without loss, indeed in many cases with gain, of heat generating ability.

In the following report, the most important results obtained in both projects are presented, beginning with chemical marker formation.

2. Chemical Markers

Although it can be shown that otherwise absent chemical compounds appear in foods as a result of thermal processing, confidence in their use and an understanding of their mechanism

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of formation would be greatly enhanced by a knowledge of their chemical composition, identity and structure. To determine the times and temperatures to which thermally processed foods have been exposed, and to relate this information to the exposure and destruction of bacteria in such foods, it is essential to know the kinetics and temperature dependence of the marker formation reaction. Following acquisition of such knowledge, a model of the dynamical behavior in thermal food processors can be undertaken, and verified by experiment. This research has contributed to each of these stages in the development of a chemical marker as an index of food sterilization, and as a more generalized index of the time-temperature histories of processed and stored food.

2.1   Isolation of Compounds Not Found in Unheated Foods

.A general analytical scheme was devised to investigate changes in carbohydrate composition in foods subjected to thermal processing. Food extracts were eluted on anion exclusion chromatography columns, which separates individual components, and monitored by photodiode array detection, which is particularly sensitive to uv light and has wavelength scanning ability. The results were displayed as three-dimensional (absorbance as functions of both retention time and wavelength) contour maps. A marker compound designated M-1 was detected in heated meats, vegetables and fruits, but not in control samples of unheated foods. Heating beef extracts yielded two markers: the aforementioned M-1 and a second, different marker designated M-2. A third marker compound, designated M-3, was detected in aseptically processed juice drinks, and in heated fruits and vegetables.

2.2   Precursors of Intrinsic Chemical Markers

To identify the precursors of markers, gel filtration chromatography was used to fractionate unheated foods and, upon heating each fraction selected for examination, markers were searched for. In addition, low molecular weight compounds known to be present in foods, such as ascorbic acid, thiamin, glucose and sucrose, were heated in solution and examined for formation of new products. The results of such studies showed that D-fructose is the precursor of M-1 and M-3. The formation of M-2 in meats involves both meat proteins and a water-soluble component. Further work is required before both precursors of M-2 can be identified.

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2.3 Identities of Chemical Markers

Marker identity was determined by gas chromatography-mass spectrometry (GC-MS). A typical procedure for M-1 began with addition of one gram of D-fructose to 9 mL of orange juice, followed by heating, filtration, and anionic chromatography of the filtrate. Peak portions corresponding to M-1were collected and evaporated. The small amount of residual material was redissolved in minimal amounts of methanol and analyzed by GC-MS. On the basis of the parent molecular weight peaks and the fragmentation patterns, assignments to compounds of known structures were made. These compounds were then tested to determine if their chromatographic, optical, and mass spectrometric characteristics were identical with the associated marker compounds. The result of these studies was establishment of chemical identities for each of the markers M-1, -2 and -3 as shown in Figure 1.
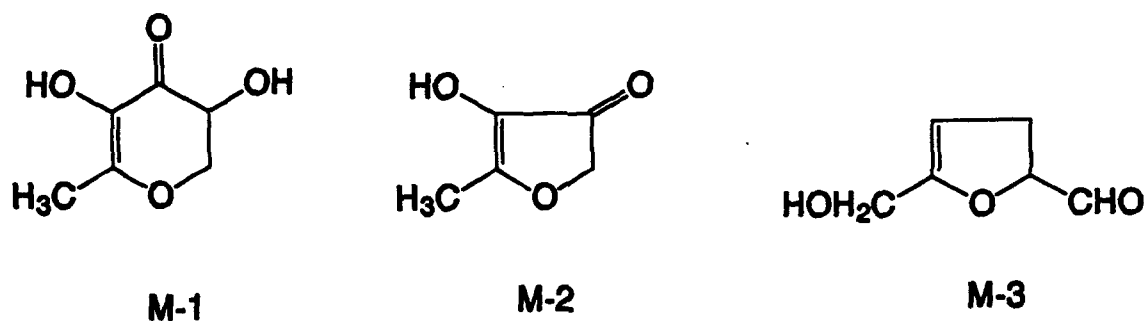

Figure 1. Structures of chemical markers. M-1, molecular weight 144, 2,3-dihydro-3,5-dihydroxy-6-methyl-4(H)-pyran-4-one; M-2, molecular weight 114, 4-hydroxy-5-methyl-3(2H)-furanone; M-3, molecular weight 126, 5-hydroxymethyl-furfural.

2.4 Kinetics and Modeling

Emphasis was placed on the kinetics of formation of M-1; M-3 behaves similarly, but the formation of M-2 shows complex kinetics and further work is being carried out with this system. The kinetics of formation of M-1 were measured at four different temperatures. At each

temperature studied, the formation exhibited first-order kinetics. Arrhenius parameters A (2.11 × 10^{11} min^{-1}) and E_a (23.7 kcal mol^{-1}) were obtained from the temperature-dependence of the rate constant. By comparison, the corresponding parameters for *Clostridium botulinum* are 7.82 × 10^{40} min^{-1} and 71.8 kcal mol^{-1} (D. Lund, 1975). To show that the marker yield may be correlated with bacterial lethality in aseptic food processing, nonisothermal conditions must be considered. One example of such a temperature profile is a temperature that is a symmetric quadratic function of time. Differential equations describing the first-order formation and destruction of marker and microorganism, respectively, and a quadratic rise and fall in temperature can be combined into a realistic dynamical model of thermal food processing.

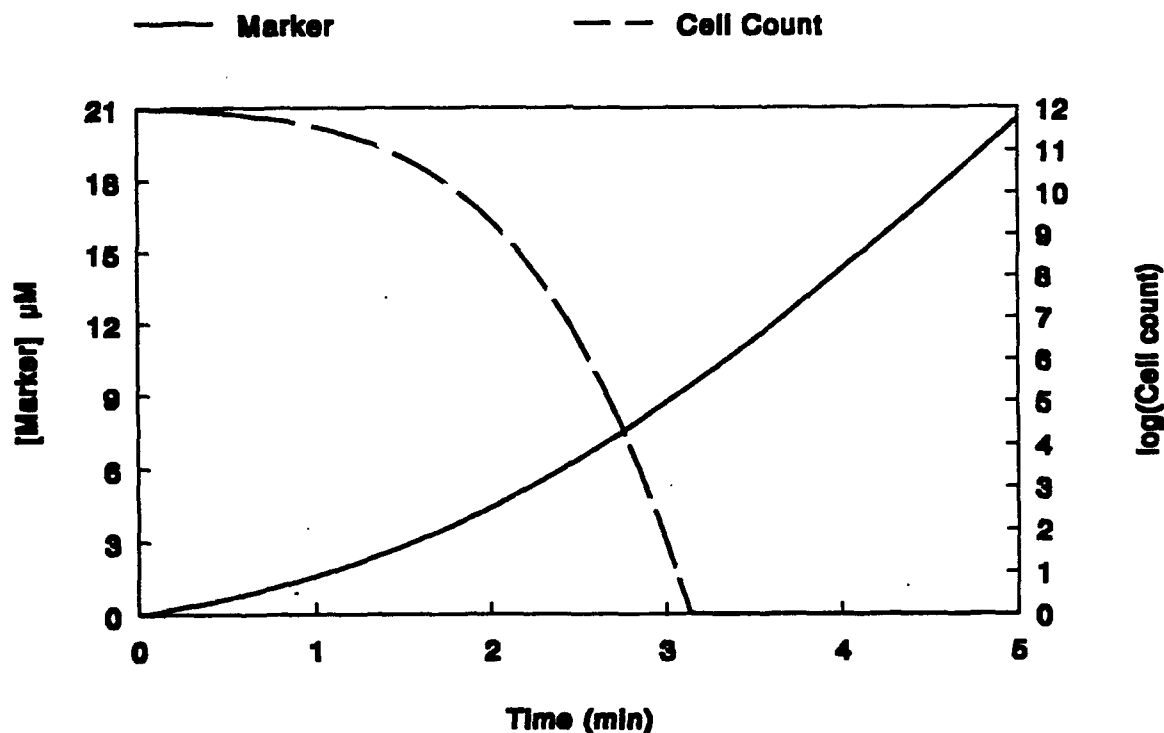These equations were integrated by a semi-implicit Runge Kutta method on a PC (Kaps

Figure 2. Kinetics of marker formation (left Y-axis) and *C. botulinum* destruction (right Y-axis) within the same solution and subject to a quadratic temperature pulse, 121°C maximum.

and Rentrop, 1979). As shown in Figure 2, the kinetics curves for marker formation and bacterial destruction exhibit dynamic responses over the same time range. A thorough treatment of this

phenomenon (Ross, 1993) indicates that there is a linear relationship between decadic reduction in bacteria population and fractional formation of a marker at a specific peak temperature. Therefore, a predictive equation of bacterial destruction based on the measured amount of marker formation is now available. This relationship was tested using microbiological data from a simulated aseptic processing procedure and using such data from inoculated samples in a commercial facility. Measurements of the logarithm of bacteria population relative to the initial inoculum population and the fractional formation of marker substantiated the linear predictive equation.

The methods of analysis worked out in this research can be applied to a wide variety of such reactive systems undergoing chemical changes in a nonisothermal environment. Applications to changes occurring in food storage with no temperature regulation, and in microwave cooking and processing of foods is currently underway.

3. Water-Activated Chemical Heaters

Literally hundreds of thousands of FRH units have been used successfully, for example, in Operation Desert Storm. This success has engendered the desire to repackage and improve this chemical heater and use it in a variety of contexts and applications where flameless heating is advantageous. Yet, little help for this task is forthcoming from either the inventor (Kuhn et al., 1985) or the several manufacturers of this product, because the intrinsic mechanism of the iron-promoted, chloride ion-catalyzed magnesium-water reaction (1) is not understood by them.

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 + heat \tag{1}$$

To solve this problem, we have used an experimental approach and gathered such data as the rates of heat and H_2 generation and the effects of degree of contact between iron and magnesium on these rates. From these data and our analyses of them, we elucidated the mechanism of reaction 1. This framework has allowed us to devise improvements of the FRH, particularly generation of heat with suppression of H_2 gas.

3.1 Methods

The active component of the FRH is Mg/Fe particles of 5 mol percent iron, which were obtained from Zestotherm Corp. We also obtained Mg/Fe particles specially milled for us by Dymatron Corp. to contain varying molar percentages of iron, milled for different periods of time. The size, shape, and distribution of the two elements in the particles were determined by scanning electron microscopy. The kinetics of heat generation were followed in a calorimeter equipped with digitized temperature output, and the kinetics of H_2 generation were followed by manually recording gas volume in a manometer attached to a closed vessel in which reaction 1 was carried out.

3.2 Mg/Fe Particle Structure and The Roles of Iron and Chloride

Reaction 1 should proceed with explosive rapidity, but in the absence of iron and chloride it is extremely slow (Cotton and Wilkinson, 1988). The sluggish rate of reaction is caused by the magnesium oxide/hydroxide surface coating which prevents water from contacting the magnesium metal surface. Our experiments indicate that the iron-promoted reaction is first-order in moles of magnesium per unit area of surface. After reaction a small but non-negligible amount of iron(III) is detectable in the spent solution. Dissolved O_2 is not a reactant. We have therefore postulated that even a slight amount of surface contact between iron and the magnesium oxide layer suffices to initiate reaction. The relatively slow but appreciable corrosion of iron produces reactive intermediates, which promotes reaction of magnesium metal, breaking the integrity of the surface coating. The reaction is catalyzed by chloride ion, and we have interpreted this result to mean that chloride keeps open the channels penetrating the oxide layer by preventing formation of MgO or $Mg(OH)_2$. A species such as Mg(OH)Cl, for example, though not thermodynamically stable, would retard formation of the oxide layer during the brief period of reaction 1. Indeed, chloride ion should facilitate further channeling by replacing OH⁻ ion in the coating.

In a test of our postulated mechanism, we compared the reactivity towards 2 M NaCl of magnesium ribbon in contact with iron wire against uncontacted magnesium ribbon. Uncontacted magnesium did not react; the strip in contact with the iron wire reacted instantly in conformity with our mechanism. Additional studies with the specially prepared particles of varying iron

contact showed that the reaction rate is linearly proportion to iron content up to about 3%, and then rapidly saturates; further increases in iron content do not increase the rate of reaction. Electron microscopical examination of the particles indicates that the smaller, harder iron particles are uniformly blended into the larger, softer magnesium particles. We conclude that milling is an essential component to preparing the chemical heating element, as it ensures rapid and uniform reaction and therefore heat generation.

3.3   Molecular Mechanism of Water Reduction By Activated Magnesium

The simplicity of reaction 1 masks the considerable complexity of the elementary reactions that give rise to the formation of molecular hydrogen. First among these reactions, we postulate, is the transfer of an electron from the metal surface to the aqueous medium, which results in a trapped and only partially solvated electron, e_p^-. One fate of this species is to become a fully solvated electron, e_s^-, a few picoseconds later. Initially, these transient entities will be located close to the reactive metal surface, but some of them will diffuse into the bulk of the solution, leading to an inhomogeneous distribution of reactive species. These heterogeneous processes then give way to bimolecular reactions of the transient species, many of which have been studied by radiation chemistry.

A reasonably complete list of such reactions, focusing on formation of Mg^{2+} ion and H_2, is as follows.

$$Mg(s.) \rightarrow Mg^{2+} + e_p^- \tag{2}$$

$$e_p^- \rightarrow e_s^- \tag{3}$$

$$e_s^- + H^+ \rightarrow H^. \tag{4}$$

$$e_s^- + e_s^- \rightarrow H_2 + 2OH^- \tag{5}$$

$$e_s^- + H^. \rightarrow H_2 + OH^- \tag{6}$$

$$H^. + H^. \rightarrow H_2 \tag{7}$$

The potential for suppressing H_2 formation lies in the possibility of finding solutes with high enough reactivity towards e_p^-, e_s^-, or $H^.$ to scavenge these transient entities, forming stable products other than H_2.

3.4 Water-Activated Chemical Heaters with Suppressed H_2 Generation

Solutes chosen on the basis of their high reactivities with solvated electrons and H-atoms (Buxton et al., 1988) have the capability of suppressing H_2 formation. For example, without any solutes added, 100 mg of Mg/Fe powder reacting with an excess of 2 M NaCl releases an amount of H_2 equivalent to a volume of 93 mL of H_2 gas at STP, measured after 30 minutes of total elapsed time. Addition of monochloroacetate ion, a relatively good electron scavenger, reduced the yield of dihydrogen by 22%. The yield of dihydrogen in the presence of trichloroacetate ion, an even better solvated electron scavenger, decreases by 40%.
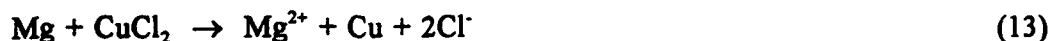
These species do not react as well with the H-atom as they do with the electron. When one adds a species such as nitrate ion, which is a good electron scavenger but only a moderately effective H-atom scavenger, the yield of H_2 is decreased further, to 78%. The effect of adding copper(II) ion, which is a very good electron scavenger and a better H-atom scavenger than nitrate ion, is elimination of all but a small residual amount of dihydrogen, the yield being decreased by 90%.

From a stoichiometric viewpoint, suppression of H_2 formation is equivalent to the occurrence of a reaction different from eq. 1. Thermochemically, the energetics are also different, and the effect on the generation of heat of a change in reaction can be quite beneficial. To illustrate, let us compare the stoichiometry and energy produced by the magnesium-copper(II) reaction with eq. 1, the magnesium-water reaction, for which 84.36 kcal/mol-Mg of energy is released. In experiments involving acidic solutions and an excess of Cu^{2+} over Mg, the copper product is elemental copper.

Mechanism:

$$CuCl_2 \rightarrow Cu^{2+} + 2Cl^- \tag{8}$$

$$Mg \rightarrow Mg^{2+} + 2e_s^- \tag{9}$$

$$2e_s^- + 2H^+ \rightarrow 2H^{\cdot} \tag{10}$$

$$H^{\cdot} + Cu^{2+} \rightarrow Cu^+ + H^+ \tag{11}$$

$$H^{\cdot} + Cu^+ \rightarrow Cu + H^+ \tag{12}$$

Overall Stoichiometry (Eq. 8 + 9 + 10 +11 +12):

$$Mg + CuCl_2 \rightarrow Mg^{2+} + Cu + 2Cl^- \tag{13}$$

For this stoichiometry the calculated heat released is 139 kcal/mol-Mg, which is almost twice that of reaction 1, in excellent agreement with experimental observation.

3.5   Scavenging Effectiveness and the Proposed Mechanism

Support for the validity of the proposed mechanism comes from scavenging experiments in radiation chemistry. Hunt (1976) has shown that in a system where a reactive species such as e_s^- is preceded by a more short-lived precursor such as e_p^-, and if both are inhomogeneously distributed, then the yield of the reactive species will be decreased by scavengers according to the equation

$$y_s/y_c = \exp(-[S]/[S]_{37})\qquad(14)$$

where y_s is the yield in the presence of scavenger, y_0 is the yield in the absence of scavenger, [S] is scavenger concentration, and $[S]_{37}$ is a constant representing that scavenger concentration at which the yield is reduced to y_0/e. This relation was found by Hunt using picosecond pulse techniques for direct measurement of the concentration of the solvated electron. Similar results were found in low temperature pulse radiolytic studies of 50:50 water:ethanediol glasses containing electron scavengers (Taub, 1969), and for the inhibition of positronium formation in systems containing high concentrations of electron scavengers (Duplàtre and Jonah, 1985). These last-named workers showed that their rate constants for positronium scavenging correlated with rate constants for electron scavenging; i.e., lower $[S]_{37}$ correlates with higher electron scavenging rate constants.

Values for four of the scavengers studied with the Mg-H_2O reaction show a reasonably good linear fit when $[S]_{37}$ is plotted against the rate constant of electron scavenging. Studies with additional scavengers are being carried out to provide a more definitive test of the postulated mechanism. However, the effectiveness with which the rate constants for electron and H-atom scavenging have been used to predict semi-quantitatively which scavengers lower H_2 yield best, indicates that the main assumption, the commonality of e_s^- in both magnesium and radiolytic reductions, is a valid and important contribution to understanding the mechanism of this fascinating and highly useful reaction system.

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Kustin, K.; Ross, E.W. *J. Chem. Ed.* 1993, *70*, 454.

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Kim, H.-J.; Taub, I.A.; Richardson, M.J.; Kustin, K.; Ross, E.W. "Intrinsic Chemical Markers for Validating the Sterility of Aseptically Processed Particulates," *Activities Report of the R &D Associates* 1992, *44*, 120.

Kim, H.-J.; Taub, I.A.; Richardson, M.J.; Yeomans, W.; Kustin, K.; "Structural Investigation of the Intrinsic Chemical Markers Formed in Aseptically Processed Particulate Foods," *Proceedings of the Fourth Natick Science Smposium 9-10 June 1992*, Herz, M.L.; Sklarsky, T.A. Eds., Technical Report Natick/TR-92/044; Natick, MA 1992, 294.

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5.3 In Press

Taub, I.A.; Roberts, W.; LaGambina, S.; Kustin, K.; "Suppression of Hydrogen Formation in Chemical Heating," Army Science Conference.

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